

PATENT SPECIFICATION

DRAWINGS ATTACHED

921.305



Date of Application and filing Complete Specification April 17, 1961.

No. 13858/61.

Application made in Germany (No. F31020 IVb/12o) on April 16, 1960.

Complete Specification Published March 20, 1963.

Index at acceptance:—Class 32, EB1H, EK2D.

International Classification:—C07c.

COMPLETE SPECIFICATION

Process for the Manufacture of Unsaturated Gaseous Aliphatic Hydrocarbons

We, FARBERWERKE HOECHST AKTIEN-GESELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate recognised under German Law, of (16) Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of unsaturated gaseous aliphatic hydrocarbons.

It has been known to produce acetylene and lower olefines by mixing gaseous or liquid hydrocarbons with a hot carrier gas and thus thermally decomposing them. The use of hydrogen, carbon dioxide, carbon monoxide, mercury vapour and also steam has been proposed as the carrier gas. The carrier gas which has been used in a great number of known processes has been heated to the required high temperature by various methods.

In a regenerative process, for example, ceramic material has been heated by combustion gases and, after having been scavenged with inert gases, the hot bricks have been used for heating steam. This process has had the disadvantage that, due to the cooling of the bricks, the steam temperature has dropped continuously so that repeated heating has become necessary, so that the reaction products have always had varying compositions. Moreover, this process has required high expenditure pertaining to apparatus, a meticulous control and has involved high losses in energy.

It has also been possible to heat the carrier gas by passing it through tubes which have been heated to a high temperature from the outside. When metal tubes have been used the temperatures have been limited, on account of the melting point, the corrosion,

and the stability of the material, to a level that has been too low for a profitable hydrocarbon cracking. The use of ceramic tubes has involved too great a loss in heat owing to the poor heat transition.

In other processes the hot combustion gases of hydrogen or low boiling hydrocarbons have been used as a carrier gas. These hot combustion gases have been particularly suitable for use in the cracking of hydrocarbons, but their price is relatively high. Moreover, in contradistinction to high boiling aliphatic hydrocarbons low boiling aliphatic hydrocarbons are more suitable for being cracked since they give high yields of unsaturated hydrocarbons while only small amounts of tarry and high boiling products are simultaneously formed, so that for this reason also it is not recommended to use them for heat generation.

Therefore, it has already been proposed to produce the hot carrier gases required for the pyrolysis of hydrocarbons by burning fuel oils and other high boiling hydrocarbons.

When, however, fuel oils and other weakly vaporizable hydrocarbons having a longer carbon skeleton have been employed, the use of which is especially favourable on account of their low price, it has been found that the velocity of the combustion has been too slow for the intended purpose. The burners used have had to be very tall in order to enable the flame to burn out in the combustion chamber. This has meant not only increased costs of apparatus but also considerable losses in heat which have been particularly considerable when combustion chambers that are cooled with liquids have been used.

Attempts have been made in industry to shorten the flame by adding the non-readily combustible oil by means of nozzles, but on account of the high viscosity of the non-readily vaporizable oils and their content of tarry constituents a complicated apparatus

has been required which has been very expensive as well as being readily liable to disturbances.

5 The desired effect of a considerable shortening of the flammability has not been obtained either by diluting the fuel oils or other difficultly combustible hydrocarbons with low boiling hydrocarbons. Moreover, this step has not been advisable, as already pointed out above, since the low boiling aliphatic hydrocarbons are more suitable for being cracked.

10 A preheating of the non-readily combustible hydrocarbons to about 400° C. has likewise not given the desired result. A preheating to higher temperatures has involved technical difficulties. When the preheating has been performed in tubes, these have quickly become clogged by a carbon-containing solid deposits. When the preheating has been carried out with heat carriers only the low boiling proportion has evaporated, while the non-readily volatile proportions have remained on the heat carriers where they have carbonized.

25 It has now been found that fuel oils, crude oils and other non-readily vaporizable hydrocarbons, especially those containing at least 10 carbon atoms, can be burned with a short flame so that they can be used for the generation of a hot carrier gas for cracking hydrocarbons, even in burners provided with liquid cooling and without any notable losses of heat occurring. The non-readily vaporizable hydrocarbons are first vaporized by injecting them into a combustion gas current having a temperature above 1500° C., and preferably above 2000° C., and cracking them and the hot gas current having a temperature of 800—1500° C., and preferably 1000—1400° C. which consists of combustion gases and cracked products is then burned with oxygen to produce the carrier gas for cracking hydrocarbons.

45 The present invention provides a process for the manufacture of at least one unsaturated gaseous aliphatic hydrocarbon, particularly acetylene and/or ethylene, by pyrolysis from at least one liquid or gaseous hydrocarbon, wherein in a first stage at least one hydrocarbon fuel, advantageously a high boiling hydrocarbon, is vaporized and cracked by adding it to a hot current of combustion gases, in a second stage the hot cracked products so obtained are burnt in the presence of an oxygen-containing gas, for example pure oxygen or air, and in a third stage the liquid or gaseous hydrocarbon to be pyrolysed is mixed with the burnt products obtained from the second stage, pyrolysed by maintaining it at a temperature above 700° C. for about 10⁻⁴ to 10⁻¹ second and chilled by a cooling agent in order to avoid further reaction. The resulting gas, for example acetylene and/or an olefine, is then worked up. If desired, steam may be added

to the burnt products obtained from the second stage before the addition of the liquid or gaseous hydrocarbon to be pyrolysed.

70 The hot flue gas used for the hydrocarbon pyrolysis is thus produced in a two-stage combustion. In the first stage (preliminary state) a preferably non-readily combustible hydrocarbon, the molecules of which generally contain at least 10 carbon atoms, is injected into a very hot flue gas current, for example one formed by the combustion of an oxyhydrogen gas, and in this stage after a residence time of 10⁻⁴ to 10⁻¹ second, which can be reached, for example, in a reaction tube, the hydrocarbon is not only completely vaporized but also subjected to thermal decomposition. The cracked products which consist substantially of acetylene, olefines, hydrogen, tar and the unreacted hydrocarbon starting material are then directly burned at a temperature well above 2000° C. in the second stage (main stage) with the amount of oxygen required for combustion.

90 Advantageously the cracked products resulting from the first stage are not allowed to cool below 800° C. before burning them in the second stage. It is preferable to introduce the cracked gas of the first stage into the second stage at a temperature of at least 1000° C. At this high temperature the tarry constituents leaving the first stage are also burnt very rapidly and with a short flame in the second stage. The high temperature is reached by using a very hot combustion gas as a fuel gas in the first stage, which gas should have a temperature of at least 1500° C. and preferably above 2000° C. When this combustion gas is mixed with a relatively small amount of the hydrocarbon to be cracked, the gas leaving the first stage still has a temperature of well above 800° C. in spite of the energy consumed for heating and cracking the said hydrocarbon. When carrying out the process of the invention it is advantageous to maintain the cracked gases of the first stage for 10⁻⁴ to 10⁻¹ second at a temperature above 800° C. before they enter the second stage where they are burnt.

115 The very hot flue gas current required in the first stage for vaporizing and cracking the slowly burning hydrocarbon may be produced by burning hydrogen, carbon monoxide, methane or mixtures of these substances with oxygen, air enriched with oxygen or gases containing considerable amounts of oxygen. It is also possible to burn gaseous mixtures containing acetylene and/or olefines. Sometimes it may be advantageous to add steam prior to or simultaneously with the addition of the hydrocarbon, but in this case the hot flue gas current should then still have a temperature of over 1500° C. In any case the very hot flue gases consist substantially of oxidation products of hydrogen and/or carbon.

The energy employed in the preliminary stage by the use of an oxyhydrogen gas or the other gases described above is high but it is entirely conserved, on the one hand in the enthalpy which the cracked products possess at the high temperature level, and, on the other, in the greater energy content of the cracked products which contain double and triple bonds. The higher energy content is indicated by a high combustion heat.

After the combustion of the cracked products in the second stage the enthalpy as well as the additional energies of the multiple bonds are available in the form of calories which can be used for cracking considerable amounts of hydrocarbons due to their high temperature level.

As an example of the greater energy content of the cracked products of the first stages as compared with the starting product the formation of acetylene from *n*-decane is quoted: 330.7 kilocalories are required for cracking 1 mol of $C_{10}H_{22}$ into 5 mols of C_2H_2 and 6 mols of H_2 while the direct combustion of 1 mol of $C_{10}H_{22}$ yields 1517 kilocalories. When, however, the 5 mols of C_2H_2 and 6 mols of H_2 formed by the cracking are burnt 1848 kilocalories are obtained, that is to say the 331 kilocalories required for the cracking are also obtained.

After having produced from the fuel oil in the first stage (preliminary stage) hot cracked gases, mainly acetylene, olefines, hydrogen and tars, the hot gases so obtained having a temperature of above $800^{\circ}C$. are burnt in the second stage with the amount of oxygen required for combustion and, on account of the very high temperature, the tarry constituents burn very readily and with a short flame.

The cracked products from the first stage should be burnt with at least the stoichiometric amount of oxygen so that the tar is simultaneously burnt. In order to maintain a reducing atmosphere in the second stage hydrogen may be added after the combustion of the cracked products from the first stage.

By the combustion in the second stage the hot flue gas is formed which is required for the cracking reaction proper (third stage) and usually has a temperature above $2000^{\circ}C$. The temperature of the flue gas may be reduced to the desired level by the subsequent addition of steam. When the level has been adjusted the hydrocarbon to be cracked is added and maintained at a temperature of at least $700^{\circ}C$. for a period of reaction of 10^{-1} to 10^{-2} second, and the reaction is terminated by chilling. When a reaction time of between 10^{-1} and 10^{-2} second is chosen, and the hydrocarbon is added in such an amount that after mixing and reacting and prior to chilling the temperature is still at least $700^{\circ}C$, ethylene is obtained as the main product. Acetylene can be produced

as the main product by employing a reaction time of 10^{-2} to 10^{-1} second and such an amount of hydrocarbon that after mixing and reacting but prior to chilling the gas temperature is still at least $1000^{\circ}C$.

The hydrocarbon to be cracked is introduced in a known manner at a temperature in the range from $25^{\circ}C$. to $400^{\circ}C$. The hydrocarbon can be introduced either in the liquid or in the gaseous state. The supply of the hydrocarbon to be cracked, the chilling of the cracked products, their separation, working up, purification and the reconnection of a partial current into the cycle can be performed according to one of the known processes.

The fuel required in the first preliminary stage (for example hydrogen, carbon monoxide, methane or mixture thereof) can be taken from the gaseous cracked products obtained at the end of the second stage, when it is not available in a more favourable manner from other sources. In addition, the cracking oils obtained in the processing of the cracked products and other difficultly utilizable hydrocarbons can be used as sources of energy in the present process by cracking them in the first stage and burning them in the second stage. As compared with a process in which exclusive gaseous substances are burnt and used for the production of the flue gas, the present process offers the advantage that the amounts of hydrogen, methane and carbon monoxide necessarily obtained in the pyrolysis of hydrocarbons can be employed to a large extent for purposes other than the process of the present invention, for example for hydrogenations, oxosyntheses and the like, whereas in many other processes they must be mainly used for the generation of the energy for the cracking reaction.

It is possible, for example, in the first stage to crack 100 kilograms of oil by burning 7 kilograms of hydrogen in such a manner that the proportion by weight of acetylene to ethylene in the cracked products is about 20:80 and the cracked gases have a temperature of above $1000^{\circ}C$. When these gases are burnt in the second stage an amount of heat of more than 1,100,000 kilocalories is obtained (after the deduction of about 5% for unavoidable heat losses) which are available in the third stage for cracking hydrocarbons. If this amount of heat were produced by the combustion of hydrogen alone, more than 35 kilograms of hydrogen would be required, that is to say more than five times the amount needed for the process of the invention. With the available 1,100,000 kilocalories, 200 kilograms of hydrocarbon could be cracked so that the proportion by weight of acetylene to ethylene is 65 to 35. Alternatively, this energy can crack 300 kilograms of hydrocarbon in a proportion by

weight of acetylene to ethylene of 30 to 70, that is to say more ethylene is formed.

A special variant of the process of the invention consists in decomposing a crude mineral oil or a purified mineral oil into a distillate and a sump phase in such a proportion that the fraction remaining in the sump yields in a later combustion in accordance with the invention the amount of heat required for cracking the distillate withdrawn at the head.

When, for example, a distillate is to be cracked in a such manner that in the cracked products the proportion by weight of acetylene to ethylene is 65 to 35, about 66% by weight of the crude mineral oil or the purified mineral oil must be distilled off while about 34% remains in the sump as residue. This residue of about 34% by weight is then injected in the first preliminary stage of the present invention into a hot flue gas current produced by burning hydrogen, carbon monoxide, methane, or mixtures thereof, where it is vaporized and cracked to a minor extent. The hot cracked products are then burnt in the second stage with the stoichiometric amount of oxygen, secondary steam is added, if desired, and finally the 66% by weight of the lighter fraction of the crude oil which has previously been distilled off is introduced into the flue gas current and thus cracked. The lighter fraction can be supplied either in liquid form by injection or in gaseous form via a preheater with or without the addition of steam.

When, however, the distillate is to be cracked in such a manner that acetylene and ethylene are present in the cracked products in a proportion by weight of 30 to 70, about 74% by weight of the starting oil is distilled off while about 26% by weight remains in the sump. The approximately 26% by weight remaining in the sump is then injected, vaporized and cracked in the first preliminary stage of the present process and burnt in the second stage when the distillate of 74% is then cracked.

By a corresponding fractional distillation of the starting product a final cracked gas having any desired composition can be produced.

The process of the present invention can be carried out in a device diagrammatically shown by way of example in the accompanying drawings. Referring to Figure 1 which is a longitudinal section of the device, in a preliminary stage (space A and B) of which space A is cooled with a liquid and space B remains uncooled and which is lined with a ceramic material, a combustion gas, for example hydrogen, methane, carbon monoxide or mixtures thereof, is introduced at 1 and burnt in the space A together with oxygen supplied at 2. Fuel oil is introduced at 3 to the hot combustion gases formed. This

oil is at once vaporized and cracked and, after having passed through the short reaction path at B, enters the second stage (space C) at 4. In the second stage the cracked products formed from the fuel oil are burnt at 4 with the oxygen supplied at 5. The oxygen should be introduced in a such manner, for example radially, that a good mixing and combustion are ensured. The temperature of the current of the hot combustion gases is then reduced in C to the temperature required for the cracking by adding superheated steam at 6. The hydrocarbon to be cracked is introduced at 7, preferably after having been preheated, and cracked in the following uncooled reaction space D which is advantageously lined with ceramic material. In E the cracked gases are cooled by chilling them with a chilling liquid, preferably water, supplied at 8 to a temperature at which they do not react further. By cooling, the cracked gases are freed from steam and the readily condensing constituents. The gases are withdrawn at 9 for being worked up while the liquid is conducted to a further processing stage at 10.

Figure 2 illustrates another possible mode of construction of a device for carrying out the process of the invention. In this case the combustion gas for the main stage comes from several preliminary stages. Figure 2a is a longitudinal section through the upper part of the device and Figure 2b a cross section along the line X—X of Figure 2a. Through the inlet Z, the hot fuel gas enters the device which corresponds, in principle, to the device represented in Figure 1. In Figures 2a and 2b the letters A—E and numerals 3 to 8 have the same meanings as in Figure 1. In contradistinction to the device illustrated in Figure 1, the device represented in Figure 2 has three preliminary stages (A+B) instead of one, which are arranged symmetrically to one another at angles of 120°, and is provided with oxygen inlets each one of which is situated between each adjacent pair of the three preliminary stages.

The process of the present invention is not limited to the device represented in Figures 1 and 2 or to cooled combustion spaces. For example, instead of the three combustion spaces illustrated in Figure 2 an arrangement having four or more combustion spaces could also be used. The technical characteristics of the device used for carrying out the present invention are not critical; the importance of the invention is the fact that gaseous mixtures are burnt that contain acetylene and olefines obtained by cracking heavy oils, and the combustion gases are used as fuel gases for pyrolytic reactions.

The following example illustrates the invention, the percentages being by weight unless otherwise stated:—

EXAMPLE

From 100 kilograms of crude oil 74 kilograms were distilled off for the later production of a cracked gas. 26 kilograms of fuel oil remained in the sump.

In a water-cooled two-stage burner as illustrated in Figure 1 2 kilograms of hydrogen were burnt in the first preliminary stage in a space A with the stoichiometric amount of oxygen; 26 kilograms of the fuel oil from the sump of the distillation were supplied at 3.

The issuing gases having a temperature of more than 1000° C. were conducted into the second stage via the reaction path B. The hot issuing gases in B contained as cracking products of the preliminary stage

10% of C_2H_2 ,
24% of C_2H_4 ,
2% of C_3H_4 ,
1% of higher hydrocarbons,
2% of H_2 ,
2% of CO ,
9% of CH_4 and

49% of unreacted tars, higher acetylenes and sulphur-containing products, without taking into consideration the steam formed by the combustion of hydrogen.

In the second stage the hot cracked products which had a temperature of more than 1000° C. were burnt at 4 with 75 kilograms of oxygen. 72 kilograms of superheated steam were then supplied at 6. The 74 kilograms of the distillate separated from the crude oil was introduced at 7. After a short time of stay in the reactor D the gases were chilled at E with finely divided water and then conducted to a further processing stage. After the condensation of the steam the issuing gas contained

1.4% of H_2 ,
2.7% of CO ,
51.7% of CO_2 ,
7.2% of C_2H_2 ,
17.0% of C_2H_4 ,
1.7% of C_3H_4 ,
3.9% of higher unsaturated hydrocarbons,
7.0% of CH_4 ,
1.5% of higher saturated hydrocarbons,
1.6% of H_2S and
4.5% of cracked oil.

The carbon dioxide and the hydrogen sulphide were derived almost exclusively from the combustion of the fuel oil.

WHAT WE CLAIM IS:—

1. A process for the manufacture of at least one unsaturated gaseous aliphatic hydrocarbon by pyrolysis from at least one liquid or gaseous hydrocarbon, wherein in a first stage at least one hydrocarbon fuel is vaporized and cracked by adding it to a hot current of combustion gases, in a second stage the hot cracked products so obtained

are burnt in the presence of an oxygen-containing gas and in a third stage the liquid or gaseous hydrocarbon to be pyrolysed is mixed with the burnt products obtained from the second stage, pyrolysed by maintaining it at a temperature above 700° C. for about 10^{-1} to 10^{-1} second and chilled by a cooling agent.

2. A process as claimed in Claim 1, wherein the unsaturated gaseous aliphatic hydrocarbon is acetylene.

3. A process as claimed in Claim 1, wherein the unsaturated gaseous aliphatic hydrocarbon is ethylene.

4. A process as claimed in Claim 1, wherein the final product is a mixture of acetylene and ethylene.

5. A process as claimed in any one of Claims 1 to 4, wherein a high boiling hydrocarbon or high boiling hydrocarbon mixture is used in the first stage.

6. A process as claimed in any one of Claims 1 to 5, wherein steam is added to the burnt products obtained from the second stage before the addition of the liquid or gaseous hydrocarbon to be pyrolysed.

7. A process as claimed in any one of Claims 1 to 6, wherein the hot current of combustion gases in the first stage has a temperature of at least 1500° C.

8. A process as claimed in any one of Claims 1 to 6, wherein the hot current of combustion gases in the first stage has a temperature of above 2000° C.

9. A process as claimed in any one of Claims 1 to 8, wherein the cracked products entering the second stage have a temperature of at least 800° C.

10. A process as claimed in any one of Claims 1 to 8, wherein the cracked products entering the second stage have a temperature of above 1000° C.

11. A process as claimed in any one of Claims 1 to 10, wherein the cracked products of the first stage are maintained at a temperature above 800° C. for 10^{-1} to 10^{-1} second before entering the second stage.

12. A process as claimed in any one of Claims 1 to 11, wherein a temperature of more than 2000° C. is produced in the second stage.

13. A process as claimed in any one of Claims 1 to 12, wherein the first, second and third stages are carried out in combustion spaces cooled with liquids.

14. A process as claimed in any one of Claims 1 to 13, wherein the hydrocarbon fuel used in the first stage is a fuel oil or a crude oil and the liquid or gaseous hydrocarbon to be pyrolysed is a low boiling hydrocarbon.

15. A process as claimed in any one of Claims 1 to 14, when carried out in an apparatus constructed and arranged and adapted to operate substantially as described

herein with reference to and as shown in Figure 1 of the accompanying drawing.

- 5 16. A process as claimed in any one of Claims 1 to 14 when carried out in an apparatus constructed and arranged and adapted to operate substantially as described herein with reference to and as shown in Figures 2a and 2b of the accompanying drawings.

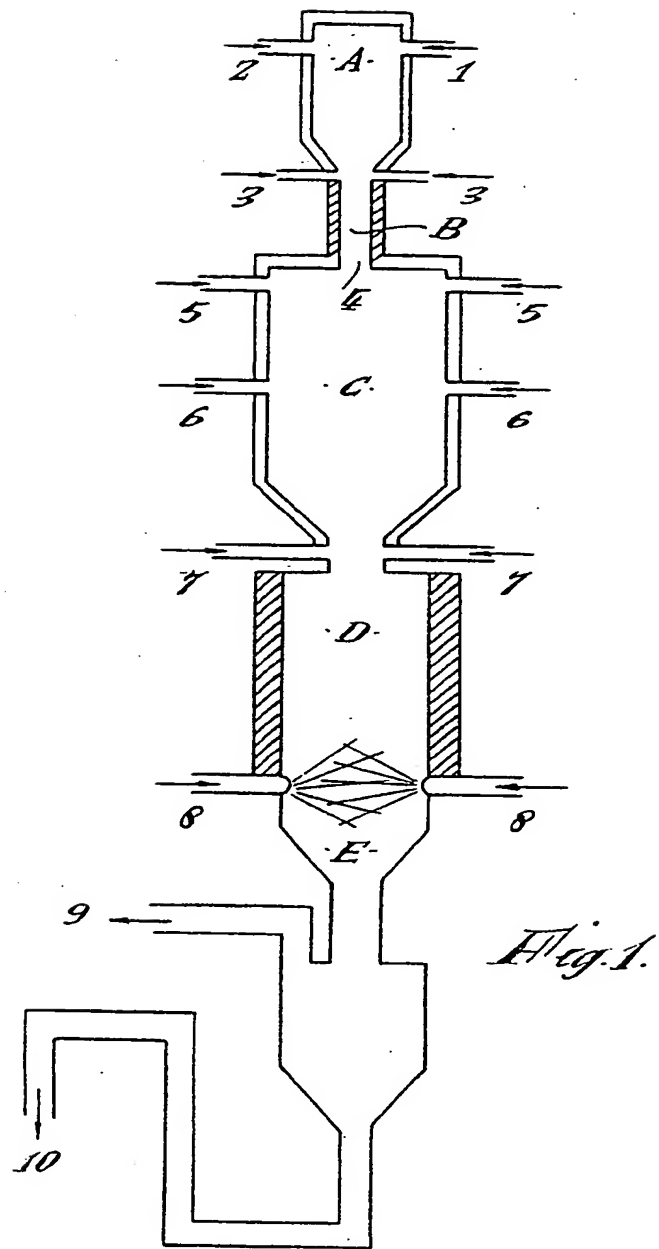
- 10 17. A process for the manufacture of unsaturated gaseous aliphatic hydrocarbons by

pyrolysis from liquid or gaseous hydrocarbons conducted substantially as described in the example herein.

- 15 18. Unsaturated gaseous aliphatic hydrocarbons when made by the process claimed in any one of Claims 1 to 17.

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.



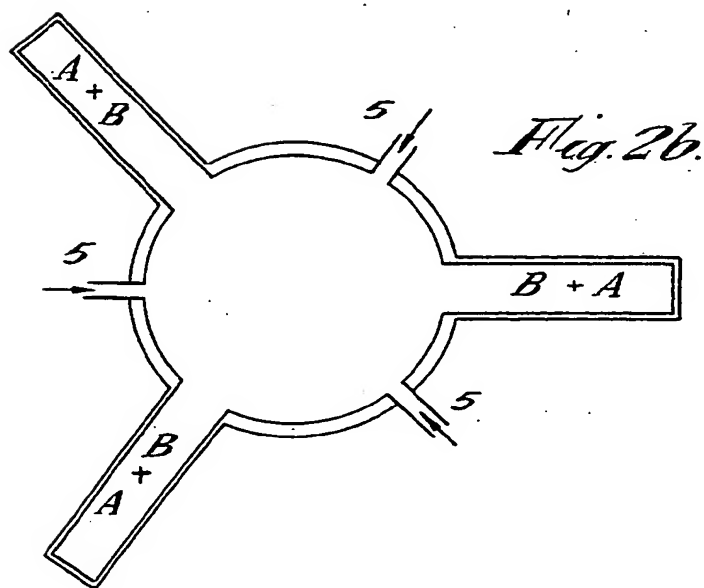
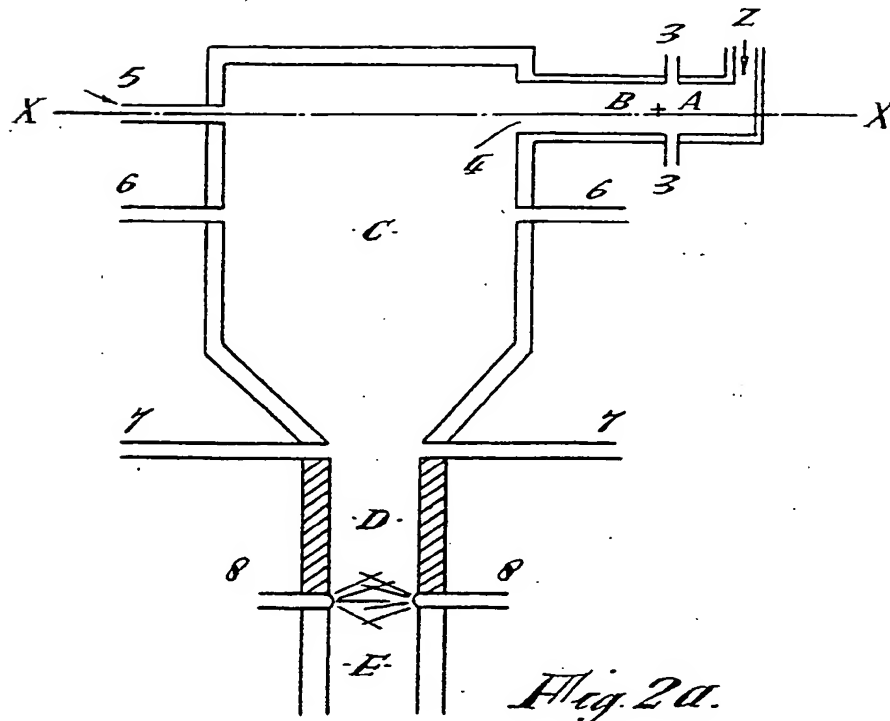
921,305

2 SHEETS

COMPLETE SPECIFICATION

This drawing is a reproduction of
the Original on a reduced scale.

SHEETS 1 & 2



921,305 COMPLETE SPECIFICATION
 2 SHEETS This drawing is a reproduction of
 the Original on a reduced scale.
 SHEETS 1 & 2

